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Polyimides for Micro-electronics Applications

Masao Tomikawa

Abstract

Polyimide is an organic polymer that exhibits the highest level of heat resistance, exhibits excellent mechanical properties and electrical insulation, and is stable for a long period of time. In addition, since it is easy to obtain polymers with different physical characteristics by changing the combination of monomers, it is possible to obtain the desired properties according to the application, and it is used in a wide range of fields such as insulating protective films for semiconductors and electronic components. This chapter describes polyimides used in microelectronics applications such as semiconductors, electronic components, displays, image sensors, and lithium-ion secondary batteries. The development of practical aspects such as photosensitivity, low-temperature curability, and adhesion to copper when used in microelectronics will be described.

Keywords: photosensitive polyimide, stress buffer, redistribution layer, poly(benzoxazole), refractive index, alignment film, pixel divided layer, planarization layer, binder resin, separator

1. Introduction (History to apply polyimide for micro-electronics)

Polyimide exhibits the highest level of heat resistance, excellent mechanical properties, and electrical insulation among organic resins, and therefore exhibits high reliability with little change in physical properties over a long period of time. Further, in general, a polyimide is obtained by reacting an acid anhydride and a diamine in a polar solvent to obtain a poly(amic acid) (PAA) as a polyimide precursor, and then converting to an inert polyimide by heat treatment [1].

Since the PAA is dissolved in a solvent or an alkaline aqueous solution, a polyimide pattern can be obtained in the state of the precursor by using such as photolithography technique.

Sato et al. examined the use of polyimide as an interlayer dielectrics for Integrated Circuit (IC) and showed that it performed higher reliability than the commonly used silicon dioxide [2]. Based on this result, polyimide has come to be used as an insulator of electronic components. Polyimides for those electronic applications required to form a pattern to make a circuit. Polyimide pattern was obtained by wet-etching process using hydrazine [3]. However, due to the toxicity of hydrazine, this method was abolished. Then partial imidized PAA was etched by tetra-methyl ammonium aqueous solution (TMAH), which is a developer of a positive photoresist. Etching of polyimide is performed at the same time as developing the photoresist. [4].

In addition, May et al. found that memory data of DRAM was broken by α rays emitted from radioactive atoms contained as impurities in the ceramic package. The issue was called “soft error” [5]. They suggested to coat pure resin on the memory cell to absorb the alpha particle. After their report, polyimide coat that high purity resin was coated on a memory cell were effective to protect the soft error.

From the viewpoint of preventing the soft error in DRAM, the coating polyimide on the semiconductor surface has been promoted [6, 7]. Further, it has been promoted to change the ceramic package to an epoxy mold resin composed to reduce a cost. The issue here is the thermal stress caused by the difference between the coefficient of thermal expansion of the semiconductor chip and the that of the epoxy mold resin. This thermal stress occurs during soldering and causes problems such as cracks in the passivation layer and epoxy mold resin, and deformation of aluminum wiring. To solve the issue, it has been proposed to apply a heat-resistant and flexible polyimide to the surface of the semiconductor chip. The polyimide layer to reduce thermal stress is called “stress buffer”. The stress buffer is the main application of polyimide coating for semiconductor devices. The polyimide for the stress buffer is required to show good adhesion to Si, mold resin and metal with rather low modulus and good thermal stability [6, 7].

To form the stress buffer, a non-photosensitive polyimide was coated and etched by alkaline solution through a photoresist as a mask. Semiconductor manufacturers have been requested photosensitive polyimide which has a capability to make a lithographic pattern by photolithographic technique, because of the high precision of patterning dimensions and the reducing patterning processes [8].

2. Negative tone photosensitive polyimide

Photosensitive polyimide was made by introducing a photosensitive group into polyimide or its precursor, or by adding a photosensitive component. The first reported photosensitive polyimide was the mixture of the dichromate compound and the PAA by Kerwin et al. [9]. Dichromate photo-resist which is composed of dichromate and water soluble resin such as PVA, casein, gelatin etc. is used in etching mask for lead frame. [10]. Reaction mechanism of the dichromate photo resist is photo induced reduction of dichromium salt [11]. However, this method has not been used because it uses a highly toxic chromium compound and the solution stability is poor.

Rubner et al. synthesized a poly(amic ester) in which a photopolymerizable acrylic group alcohol was introduced into the carboxyl group of the PAA by an ester bond and obtained negative working photosensitive polyimide [12]. This method requires acid chloride in the reaction of dicarboxylic acid and diamine, which has drawbacks such as complicated synthesis process, removal of impurities, and difficulty in removing photosensitive components during thermosetting. However, the technology was transferred to a polyimide manufacturer, and as results of vigorous research, it was widely applied in semiconductor stress buffer [13].

As a technology to counter the ester type, Hiramoto et al. have developed a simple negative photosensitive polyimide called “ionic bonded type”. The photosensitive polyimide is composed of PAA, tertiary amine having photo reactive group such as acrylic group [14]. The photo reactive group was introduced PAA by ionic interaction between carboxylic acid and tertiary amine. This method is extremely easy to obtain photosensitive polyimide, and not only the photosensitive component easily volatilizes during thermosetting, but it also acts as a catalyst for imidization, and curing is completed at a lower temperature. The ionic photosensitive polyimide was first practical use as an interlayer dielectrics for mounting substrates of super

computers [15]. In addition, this photosensitive mechanism was unclear because no reaction of photoreactive acrylic groups was observed, but it was found that PAA causes photocharge separation with ultraviolet rays and the reaction proceeds [16].

Another negative type is a soluble polyimide composed of a benzophenone tetracarboxylic acid and a diamine having an alkyl group at the ortho position which was developed by Pfifer et al. [17]. The photosensitive mechanism of this polyimide was investigated by Horie et al., And the reaction mechanism was shown in which benzophenone was excited by ultraviolet rays (UV) to cause hydrogen abstraction from the alkyl group to crosslink and insolubilize it [18].

Furthermore, Omote et al. provided a negative-type image by adding a nifedipine to PAA [19]. The nifedipine changes its chemical structure and basicity by UV exposure. The interaction between PAA and nifedipine was changed by UV exposure due to basicity change of the nifedipine [19].

3. Positive tone photosensitive polyimide

There are two types of photoresists, a negative type and positive type. Exposed area of the negative type resist came to insoluble by UV induced chemical reaction. On the other hand, that of positive photoresist came to soluble to alkaline solution by UV reaction. The negative type was first put into practical use, and then the positive type came out. Generally, in the negative type, an UV reactive group such as an acrylic group photopolymerizes with UV to form a crosslinked structure, so that the negative type is insoluble in a developing solution. It is difficult to form a fine pattern because the cross-linked polymer swells in the developer.

On the other hand, common positive photoresist is composed of novolak resin having a phenolic hydroxyl group soluble in an alkaline aqueous solution, and diazonaphthoquinone compound. The diazonaphthoquinone compound is insoluble in alkali and formed a complex with novolak resin before UV exposure. The diazonaphthoquinone compound converts to indenecarboxylic acid by UV exposure [20]. The indenecarboxylic acid is alkaline soluble. As a result, unexposed area is hard to soluble to alkaline solution and exposed area is soluble to alkaline solution [21]. The development of polyimide of this technology was also studied from an early stage, and Loprest et al. invented a positive photosensitive polyimide precursor using a PAA and a diazonaphthoquinone compound [22]. However, a good image cannot be obtained because the solubility of PAA to an alkaline aqueous solution is too large, and it has not been put into practical use as it is. The flow of this technology was subsequently announced by adding a diazonaphthoquinone compound to a polyimide or poly(amic acid) ester having a phenolic hydroxyl group [23–25]. In addition, Tomikawa et al. developed a partial esterification of PAA by using dimethylformamide dialkyl acetal. And the reaction made it possible to control the dissolution rate of the partial esterified PAA to alkaline solution. [26].

Rubner et al. developed a positive heat-resistant material using polybenzoxazole (PBO) precursor as a heterocyclic polymer having heat resistance comparable to that of polyimide [27]. The precursor of PBO is polyhydroxyamide (PHA), which is a polyamide having a phenolic hydroxyl group, and has an appropriate alkali solubility. By adding a diazonaphthoquinone diazide compound to PHA, positive image of PBO was obtained. This technology has been deployed to various companies such as Sumitomo Bakelite and is widely used [28].

In addition, the development of positive photosensitive polyimide was also considered from another point of view. Kubota et al. announced a product using o-nitrobenzyl ester of PAA [29]. This is because the o-nitrobenzyl group is eliminated by deep UV exposure, so that the exposed part becomes PAA and becomes

alkali-soluble. Furthermore, in the case of adding a nifedipine compound to the PAA developed by Omote et al. explained in the negative type, the hydrogen bonding strength changes depending on the baking conditions after exposure, and a positive type image can be obtained by controlling baking after exposure [30].

In addition, Tamura et al. found that a positive image can be obtained by baking an ion-bonded photosensitive polyimide at 130–150° C after exposure [31]. Regarding this mechanism, the glass transition temperature (T_g) differs between the exposed area and the unexposed area, and the T_g of the exposed area is slightly higher compare to that of unexposed area. When baking is performed near T_g , imidization rate of exposed area is slower than that of unexposed area due to T_g difference. High T_g , imidization of the exposed area with high T_g does not proceed, and imidization of the unexposed part with low T_g progresses, so that the exposed area with high T_g becomes an alkaline developer. It was found that a positive image was obtained [32].

The mainstream of current photoresists is chemical amplification type which is composed of alkali soluble resin protected by acid cleavable group and photo acid generator (PAG). An acid is generated from PAG by UV exposure and de-protection of acid cleavable group proceeds. Then the exposed area became alkaline soluble. This technology was also applied for polyimide. So solvent-soluble polyimide having a phenolic hydroxyl group, which was protected by an acid-cleavable protective group such as a t-BOC (tert-butoxycarbonyl) group and photo acid generator (PAG) [33, 34]. Nakano et al. developed the composition of PAA oligomer and a methylol compound are crosslinked at the time of prebaking and cleaved with an acid generated from PAG after UV exposure to obtain a positive image [35].

Furthermore, Ueda et al. proposed a ternary system using a acid cleavable dissolution inhibitor and a PAG to enhance dissolution contrast between exposed and unexposed areas and to use polyimide and PBO precursors as they are. [36]. According to this method, it is not necessary to protect the polymer itself, and by adding a dissolution inhibitor with a protecting group that is eliminated by acid, the dissolution rate ratio between the exposed and unexposed areas may exceed 2000.

Ohyama obtained positive photosensitive polyimide by reaction development patterning. [37]. In addition, they are obtained positive photosensitive polyimide from polyetherimide (Ultem), which is alkali insoluble thermoplastic polyimide, a diazonaphthoquinone compound. They designed a development solution also by mixing aqueous TMAH aqueous solution, a NMP as a solvent and a nucleophilic base such as monoethanolamine to proceed decomposition. As a result, they obtained a positive polyetherimide image [38]. Furthermore, it was shown that engineering plastics such as polycarbonate can be used in this method [39]. They investigated and stimulated development mechanism and found that a salt composed of an acid made of a diazonaphthoquinone compound and an alkali of the developer accelerates the penetration of the hydrophilic developer into the exposed area. The nucleophilic reaction in the exposed area proceeds, and the main chain is decomposed. On the other hand, it has been reported that the unexposed area does not form salt in the developing solution and the reaction of the main chain is negligible, so that the unexposed area remains [37]. This technique can also obtain negative images, which was obtained by adding phenylmaleimide and diazonaphthoquinonediazide compounds to the polymer, and developing with a developer containing alcohol in a TMAH aqueous solution [40]. Furthermore, it has been reported that development with an aqueous solution of TMAH, which is generally used in semiconductor processing, is also possible [39]. This method is an interesting technique because it shows that a polymer having more excellent physical properties can be applied as a photosensitive materials. It has also been reported that even when a polyisoimide and a diazonaphthoquinone compound are added, the exposed portion becomes alkali-soluble and an image is obtained [41].

4. Low temperature curable photosensitive polyimide

New photosensitive polyimide applications have emerged for semiconductor packages in addition of stress buffer. As semiconductors and electronic components are becoming smaller, the boards on which they are mounted are also becoming smaller, and the components are placed on the board and heat-mounted from the method of inserting the pins as electrodes into the holes in the printed circuit board (PCB). Surface mount technology (SMT) has been developed to minimize the footprint of semiconductors and electronic components [42]. In SMT, the substrate on which semiconductors and electronic components are mounted is raised to a temperature at solder melting, and mounting is performed. Therefore, in semiconductors with not so many electrodes, chip scale packages (CSPs) have emerged in which the electrodes are formed into convex bumps at the bottom rather than around the semiconductor [43]. In addition, for those with many lead-out electrodes, bump formation is not sufficient with the semiconductor package alone, and a fan-out type package (FO-WLP) that enables bump formation even in the mold resin portion has appeared [44]. For both CSP and FO-WLP, a re-distribution layer (RDL) is formed using photosensitive polyimide or PBO so that bumps can be formed using the entire surface of the semiconductor package [45, 46].

To make a FO-WLP, RDL is formed outside the chip (**Figure 1**). Therefore, the chip is put into the mold resin, and rewiring is also formed in the mold resin portion. Therefore, the material used for rewiring needs to be formed below the heat resistant temperature of the mold resin composed of epoxy resin and silica filler.

As a result, materials that can be fired at 200° C or lower are required for rewiring applications. Furthermore, in FO-WLP, since photosensitive polyimide and PBO are directly bonded to LSI and mold resin, it is necessary that the photosensitive polyimide, PBO and solder bumps are not destroyed by thermal shock due to the difference in thermal expansion coefficient. Mechanical properties such as elongation at break are regarded as important, and product development is being carried out for this purpose [47]. In addition, FO-WLP is becoming finer, and wiring is being formed with a line and space of 2 μm [48].

Various studies have been conducted for low temperature curing. In order to perform imide ring closure at a low temperature, a thermobase generator is added [49], and an pre-imidized polymer is used [47]. In addition, focusing on the main chain structure of polyimide, Sasaki reported that the imidization rate determined by the acidity of the diamine component. So diamine having high acidity gave low temperature imidization [50].

Furthermore, PBO is also being studied for low temperature cyclization. If the structure constituting PBO is made flexible, low temperature curing is possible [51], and a thermoacid generator that generates sulfonic acid by heat is added. It has been reported that it cyclizes at low temperatures [52]. Furthermore, Kusunoki

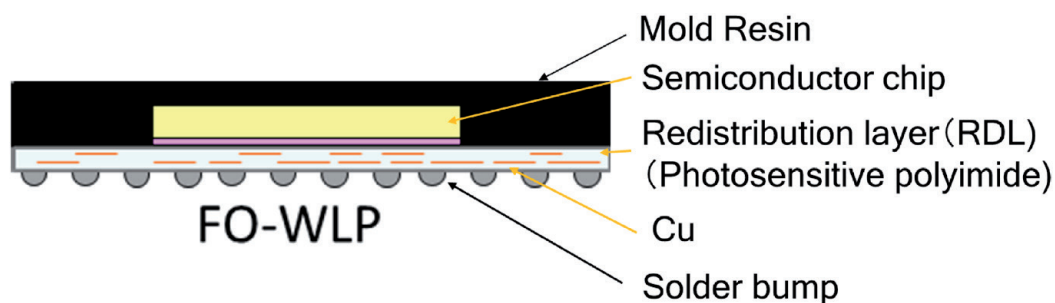


Figure 1.
 Cross section structure of FO-WLP.

reported photosensitive polynorbornene which has low modulus, low dielectric constant, low water absorption with low temperature curable [53].

5. Polyimide for image sensor

As the image sensor becomes smaller and more integrated, each pixel becomes smaller, the amount of incoming light decreases, and the sensitivity decreases. On the other hand, a micro-lens is formed on the pixel to increase the light flux. Suwa et al. dispersed titania sol in a positive photosensitive polyimide to obtain a positive photosensitive heat-resistant resin having a refractive index of 1.9. This material is further made lenticular in the curing process [54]. In addition, they developed a siloxane base photosensitive high refractive index material whose refractive index is 1.9 [55]. On the other hand, Oishi et al. focused on the triazine skeleton, and obtained a material having a refractive index of 1.80 by using a hyperbranched polymer of triazine without adding a filler having a high refractive index [56].

6. Polyimide for LCD

One of big applications of polyimides to a display is an alignment layer of a liquid crystal display (LCD). The purpose of alignment film is arranging liquid crystal molecules in LCD (**Figure 2**). The alignment film is rubbed by a cloth to align liquid crystal molecules. Although the detailed mechanism by which the rubbing-treated polyimide orients the liquid crystal molecules is unknown, it was found that the polyimide is suitable as a liquid crystal alignment film, and it has come to be used in liquid crystal displays. Initially, aromatic polyimides such as PMDA and ODA were used for the alignment film of TN (Twisted Nematic) type LCD. Then STN (Super Twisted Nematic) type LCD was developed. New polyimide was developed for STN LCD alignment film [57].

To widen the viewing angle VA (Vertical Alignment) type, and IPS (In Plane Switching) type LCDs were shown [58].

To improve the LCD, numerous studies have been conducted on the relationship between the alignment state of the liquid crystal and the alignment film from the viewpoint of the influence of the rubbing treatment and the molecular structure of polyimide [59–62]. Furthermore, after that, a series of systematic basic studies were conducted using synchrotron radiation equipment [63–66].

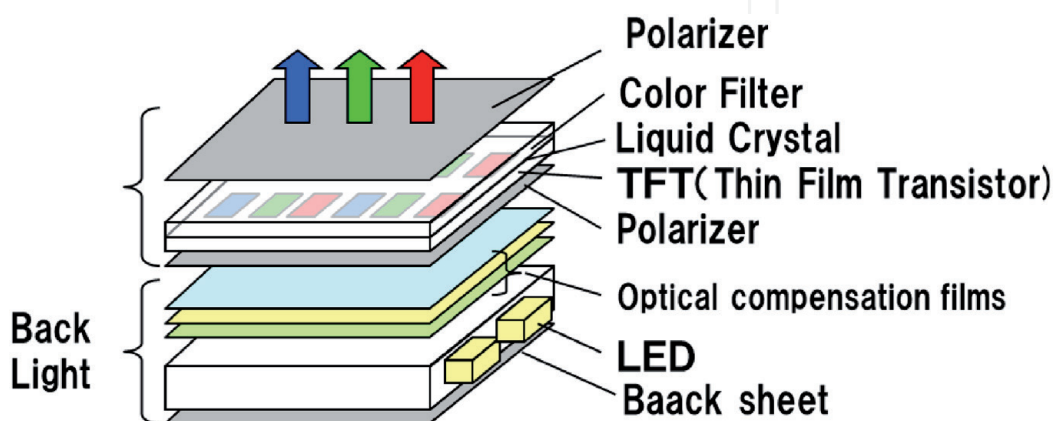


Figure 2.
Cross section structure of Liquid Crystal Display.

From those basic studies design guides for the alignment film were shown [67]. Various types of polyimide alignment materials were commercialized [68].

Since dust is generated in the rubbing process, a method of aligning the liquid crystal without rubbing has been studied [69]. Photo active polyimide were suggested for the phot rubbing process. Photo active polyimide means photo rearrangement type and photo decomposed type [69–72].

7. Polyimide for OLED

Compared to LCD, organic EL displays (OLED) are self-luminous, have a large contrast between emitting area and non-emitting area, have a simple layer structure and can be made thin, have a fast response speed, and can display even on flexible substrate. The cross-sectional structure of the OLED is shown in the **Figure 3**. There are electrodes above and below the emission layer, and the light emitting layers are separated from each other by a pixel divided layer (PDL). Since the PDL contact with the emission layer, The water and decomposed gas generated from the PDL damage the adjacent to emission layer, narrowing the light emitting region. Heat resistance and degassing properties are important. In addition, the partition wall is not like a rectangular parallelepiped, but a trapezoidal shape with a gentle taper is preferable to suppress the current concentration.

On the other hand, another organic resin in OLED is PNL (Planarization Layer). The PNL is also required low out gas and moisture. Therefore, a positive photo-sensitive polyimide material is suitable as a PDL and PNL for OLED display and is widely used [73].

8. High frequency application

In the future, mobile phones will be able to send and receive large amounts of data in a short time by utilizing high frequencies, the operating frequency of application processors that control mobile phones to become multifunctional will be higher, and automobile collision safety. Due to the increasing adoption of millimeter-wave radar to improve performance, the use of high-frequency materials will increase more than ever. For those applications, materials such as fluoropolymer [74], liquid crystal polyester [75], BCB (benzocyclobutene) [76], polyphenylene ether [77], and cycloolefin polymer [78] have a dielectric constant in the high frequency region. It has been used because of its low dielectric loss, but there are also problems such as low adhesiveness, and low dielectric constant and

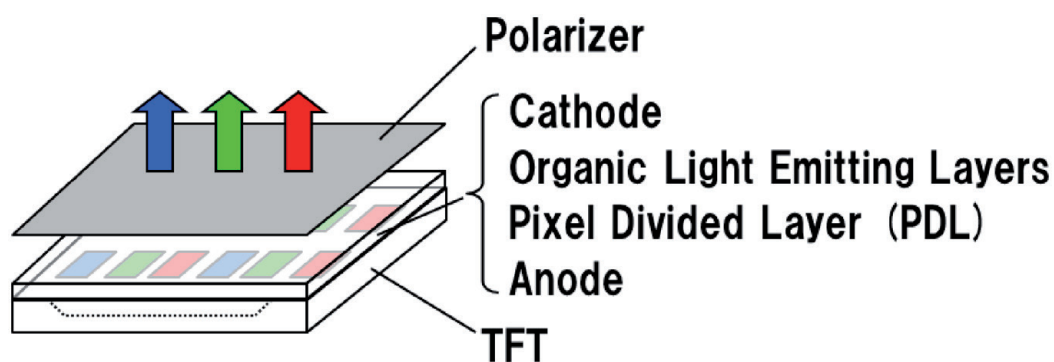


Figure 3.
Cross section structure of OLED display.

low dielectric loss are being studied by making porous polyimide [79]. Authors obtain a low dielectric loss photosensitive polyimide design guide line by dynamic mechanical analysis [80].

9. Li ion battery

Lithium-ion secondary batteries (LiB) are used widely as high energy density storage batteries for mobile phones, notebook PCs, electric tools, electric vehicle and so on, due to their high discharge voltage, almost no memory effect of charging and discharging, and small self-discharge. The battery is composed of negative electrode (Anode), positive electrode (Cathode), separator, and electrolytic solution as shown in **Figure 4**. Anode is composed of anode active material, binder resin, and Cu foil. Cathode is composed of cathode active material, and Al foil. SBR (styrene butadiene rubber), PVDF (Polyvinylidene fluoride) are used for binder resin. Conductive assisting agent is added to decrease electric resistivity in binder resin. Current anode acting material is carbon-based materials such as graphite or hard carbon. Lithium ions move in and out between the layers of graphite to charge and discharge, and the theoretical capacity is 372mAh / g. Recent batteries have almost reached this theoretical value, and it is necessary to change the active material to further increase the capacity. Silicon is attracting as an anode active material candidate for next generation due to its large capacity [81]. However, the volume changes of the Si active material is about 400% at charging / discharging. To use large volume change Si material, new binder resin is required to endure the big volume change. Promising candidate is polyimide which has excellent mechanical properties and good adhesive properties. It has been reported that the cycle characteristics are significantly improved when a polyimide-based material is used as a binder for such a Si base large-capacity anode active material [82–84].

On the other hand, Li metal oxide base material is used for cathode active compound. Common binder resin for cathode active material is PVDF. To improve the safety, olivin compound such as LiFePO_4 (LFO) is developed [85]. Li ion capacity of LFO is small compare to Li metal oxide material such as LiCoO_2 , LiNiO_3 . But LFO shows higher thermal stability than those of Li metal oxides. So operation temperature of LFO is wider than that of Li metal oxide. Miyuki et al. reported that polyimide is good binder for LFO due to high temperature operation, high charging / discharging property [86].

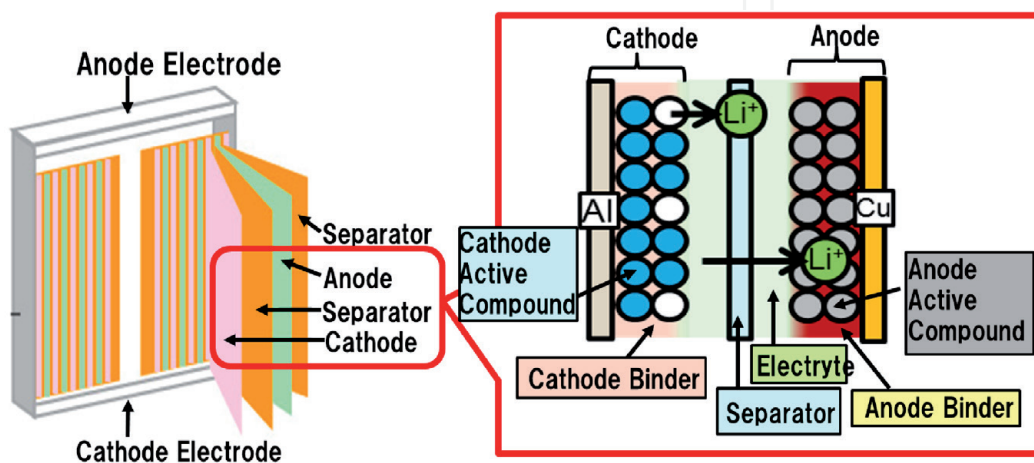


Figure 4.
Schematic diagram of lithium ion secondary battery.

In addition, porous polyimide separator was obtained from polyimide and silica filler. The separator shows high rate and long term stability [87].

10. Conclusion

It has been more than 50 years since polyimide was put into practical use, but development for new applications is still underway. This is due to the high degree of freedom in design that allows the material called polyimide to be easily synthesized, maintains excellent heat resistance, and changes other physical properties in various ways. It is expected that new developments will continue in the future due to the degree of freedom in design and excellent characteristics such as heat resistance and insulation.

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